MATERIALS
SCIENCE

Heterogeneous polyvinylchloride blends with chlorinated polyethylene: rheological, diffusion, and gas sorption characteristics

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Abstract. Rheological and diffusion properties of binary PVC–CPE blends were investigated. The blends were obtained in a rather wide composition range (PVC : CPE = 100/0, 90/10, 80/20, 60/40, 40/60, 20/80, 10/90, 0/100 wt./wt.%). It was concluded from the sorption analysis data that for coating and barrier materials systems with higher PVC content should be regarded more appropriate because of their smaller diffusion coefficients. The rheological analysis showed that all the PVC compositions with CPE were thermoplastic in nature and could be processed and recycled with traditional thermoplastic processing equipment.

Key words: thermoplastic materials, PVC, CPE, blends, rheological properties, sorption properties, structure.

INTRODUCTION

Use of thermoplastics as effective corrosion-resistant materials for coating applications and replacement of traditional materials in the automotive and building industries has gained considerable interest from both industrial and academic sectors. Such materials should possess good processability and barrier properties together with excellent mechanical characteristics. One of the most attractive ways of developing materials for the afore-mentioned applications is melt blending of two or more distinctive polymers. The blending of an engineering grade resin, such as polyvinylchloride (PVC), with an elastomer, for example, chlorinated polyethylene (CPE), can give several positive results: (1) CPE is non-volatile and does not migrate if blended with PVC; therefore compositions with CPE have a considerably longer service life than PVC alone; (2) addition of CPE to PVC reduces its brittleness, raises impact strength and fire resistance, and improves other properties; (3) addition of PVC to CPE, in turn, upgrades its barrier characteristics as well as stress–strain behaviour.

EXPERIMENTAL

The polymers PVC (C-7058-У, Russia) and CPE (CPE3614A, Dow Chemical Co) were melt blended in a rather wide composition range (PVC : CPE = 100 : 0, 90 : 10, 80 : 20, 60 : 40, 40 : 60, 20 : 80, 10 : 90, 0 : 100 wt./wt.%) by using a Banbury type mixer. The samples for rheological as well as sorption tests were prepared by compression moulding. The samples for the investigation of mass transfer properties were specifically treated in order to reduce intermolecular stresses developing in the test samples during compression moulding. The rheological characteristics of the compositions were measured on a capillary viscometer. The sorption characteristics of the low molecular polar solvent (acetone) were evaluated on a McBain-Bakr quartz spring balance. The diffusion characteristics of the low molecular compound (CO_2) were measured on specially designed testing equipment. Sorption experiments were carried out at different partial pressures (ranging from 0.10 to 0.60) and temperatures (30–60 °C). Various mathematical models, including those of mixture rule, Maxwell and Robinson, were used for the prediction of sorption properties of the PVC–CPE blends.

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RESULTS AND DISCUSSION

Viscoelastic properties of the investigated blends were characterized by the well-known rheological relationship [1]:

$$\lg \tau_W = \lg K + n \lg \dot{\gamma}, \qquad (1)$$

where τ_W – shear stress; $\dot{\gamma}$ – shear rate; n – flow behaviour index; K – consistency.

As shown in Fig. 1, the relationships of the shear rate to the shear stress of the investigated PVC–CPE blends show a typical pseudoplastic behaviour. Consequently shear stress of the compositions, depicted in logarithmic coordinates, increases linearly with the growth of the PVC content in the blend.

Pseudoplasticity of the investigated systems is evaluated by means of the flowing index, which is shown in Fig. 2. As one can see, the pseudoplasticity of the PVC–CPE blends is considerably increased by rising the PVC content in the blends, especially at higher temperatures and PVC content above 20 wt.%.

Important information about the structure of the blends can be obtained from the changes in the flowing process activation energy E_R, which are shown in Fig. 3. Irregularly arranged chlorine atoms in the CPE macromolecules promote at defined processing temperatures the flowing of the CPE-rich blends in comparison to PVC-rich blends, i.e., E_R of the polymer systems decreases with increasing CPE content in the blend. Nonlinearity of the E_R dependence on the blend content could be explained, to a certain extent, with structural changes in the polymer melt as a result of which the intermolecular interaction is weakened and the flow is promoted. These structural characteristics undoubtedly influence also relaxation processes in the polymer, as is shown in Fig. 3.

Before the investigation of the sorption properties of the PVC–CPE blends, optimal processing conditions for the manufacturing of the test samples in the form of ca. 100 μ thick rectangular plaques were determined. It was found that the optimum processing temperature was 170 °C and the optimum processing pressure 5 MPa, but the optimum compression moulding time varied from 120 to 140 s depending on the composition of the blends. Simultaneously it was determined that before sorption experiments equalization of the intermolecular stresses, created during the compression moulding of the test plaques, is necessary and can be achieved by holding the test samples in the saturated vapours of the current penetrant at least for 24 h with subsequent drying in a vacuum oven for 72 h, and final elimination of the penetrant traces to constant mass in the gas diffusion equipment.
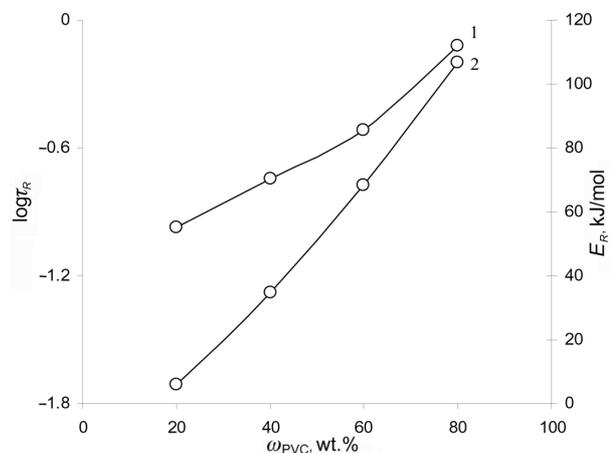
It was realized during the sorption experiments that the diffusion of the low-molecular penetrant in the investigated polymer systems with a low PVC content
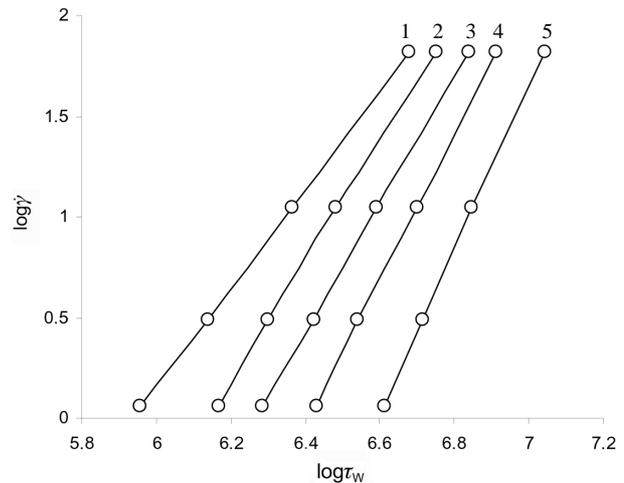
Fig. 1. Flowability curves of the PVC–CPE blends: 0 : 100 (1); 20 : 80 (2); 40 : 60 (3); 60 : 40 (4); and 80 : 20 (5) wt./wt.% at 433 K.
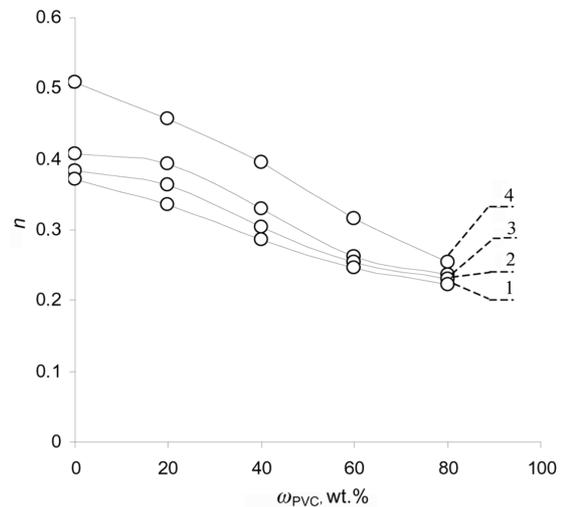
Fig. 2. Dependence of the flowing index n on the PVC content ω_{PVC} at 433 (1), 443 (2), 453 (3), and 463 K (4).

Fig. 3. Dependence of the activation energy E_R (1) and the relaxation time τ_R (2) on the PVC content ω_{PVC}.

(below 20 wt.%) can be sufficiently well described by Fick's law [2]:

$$\gamma = \frac{M_t}{M_\infty} = 4\left(\frac{D \cdot t}{l^2}\right)^{1/2}\left(\frac{1}{\pi^{1/2}} + 2\sum_{n=0}^{\infty}(-1)^n erfc\frac{n \cdot l}{2 \cdot (D \cdot t)^{1/2}}\right),$$ (2)

where D – diffusion coefficient; M_t and M_∞ – amount of the absorbed penetrant at time t and at the equilibrium state, respectively; l – thickness of the polymer film.
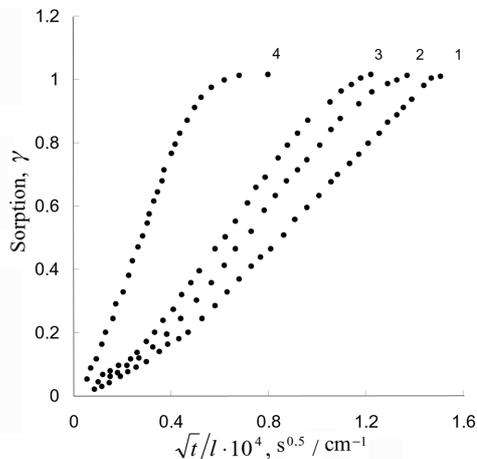
By increasing the concentration of the polar penetrant in the polymer, a rapid increase of the diffusion coefficient D was observed. This is characteristic of polymers at temperatures above their glass transition (in this case the matrix is CPE with its glass transition at about 255 K [3]).

At a higher PVC content (above 20 wt.%) a certain deviation from traditional Fick's sorption was observed. As an example, the kinetics of the penetrant sorption in the CPE:PVC = 20:80 blend is shown in Fig. 4. It can be clearly seen that at relative pressures below 0.44 the kinetics of the penetrant sorption is of anomalous character [4], which is typical of penetrant diffusion in the polymers in glassy state [2,4] and is connected with the time dependence of the penetrant diffusion rate in the volume of the polymer. Most probably this is connected with the influence of the relaxation processes, whose rates are comparable or lower than those of diffusion.

The mass transfer rates in such systems are traditionally described by means of the modified Fick's law [5]:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left[D - \frac{\partial c}{\partial x} - V \cdot C\right],$$ (3)

where V – rate of the moving polymer front, swollen in the penetrant; C – concentration of the penetrant; x – length of the diffusion path.

Consequently, the change of the penetrant concentration at a distance x from the surface of the test specimen in the fixed time periods can be written as:

$$C(x,t) = \frac{C_0}{2}\left[e^{x \cdot V/D}erfc\left(\frac{x+V \cdot t}{2\sqrt{D \cdot t}}\right) + erfc\left(\frac{x-V \cdot t}{2\sqrt{D \cdot t}}\right)\right],$$ (4)
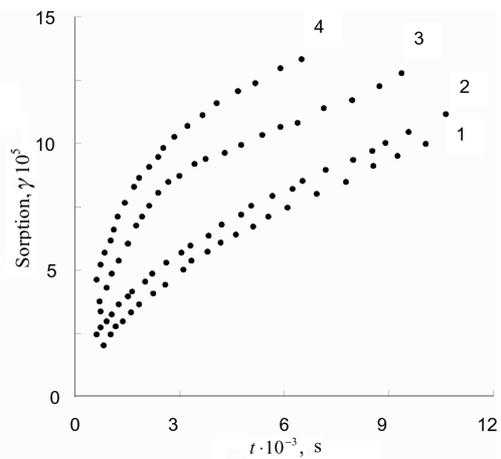
where C_0 – surface concentration, which is assumed to be constant [5].

At sufficiently great t values, which are quite realistic at carrying out sorption experiments, the amount of the absorbed penetrant can be expressed in the following way:

$$M_t = C_0\left[\frac{D}{V} + V \cdot t\right].$$ (5)

Figure 5 depicts sorption curves of the CPE20–PVC80 composition in the coordinates of Eq. (3). The values of V obtained in the current experiment fit well with the results of Kwei et al. [6], who investigated acetone absorption in glassy PVC, and Jacques and Hoppenberg [7], who investigated *n*-hexane diffusion in glassy polystyrene blends.

It is well known [8] that molecules of the penetrant can cause certain plasticization of the polymer, i.e., when the concentration of the penetrant increases, the glass transition temperature of the polymer will decrease. In the current case, at sorption values of 2, 5, and 10×10^{-5} kg/kg, the glass transition temperature of PVC was 346, 337, and 324 K, respectively. It should however be mentioned that, similarly to the penetrant, CPE can play a certain plasticizing role in the investigated systems. Consequently, the plasticizing effect becomes more pronounced with increasing CPE content in the blends (Fig. 6). For example, in the case of PCV the value of D rises by 1.5 orders when the con-

Fig. 4. Kinetics of the acetone vapour sorption in the composition CPE:PVC = 20:80 at p/p_0 0.12 (1), 0.22 (2), 0.32 (3), and 0.44 (4).

Fig. 5. Kinetics of acetone vapour sorption for the composition CPE:PVC = 20:80 at p/p_0 0.12 (1), 0.22 (2), 0.32 (3), and 0.44 (4).
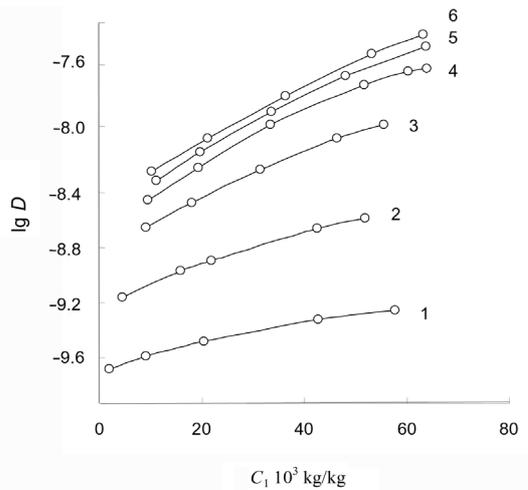
Fig. 6. Concentration dependence of the mass transfer rate (D, cm^2/s) in the compositions CPE : PVC = 0 : 100 (1), 20 : 80 (2), 60 : 40 (3), 70 : 30 (4), 90 : 10 (5), and 100 : 0 (6).

Fig. 7. Diffusion coefficients (D, cm^2/s) of the polar low-molecular compound penetration in the investigated PVC–CPE compositions: points – experimental data; curves (1), (2), and (3) – calculations according to Eqs (6), (8), and (7), respectively.

centration of the penetrant increases from 0.0091 to 0.04 kg/kg, but in the case of CPE, by 5.5 orders.

Change of the diffusion coefficient as a function of the mass content of the investigated compositions is shown in Fig. 7. The diffusion coefficient, depicted in Fig. 7, was obtained from the extrapolation of the respective curve to the zero penetrant concentration ($D_{C1=0}$), at which the plasticizing and thermodynamic effects of the penetrant are minimal. Additionally to the experimental data, Fig. 7 demonstrates also results of the theoretical calculation according to the following well-known relationships [9]:

$$D = \varphi_1 D_1 + \varphi_2 D_2 \quad \text{(additive model),} \qquad (6)$$
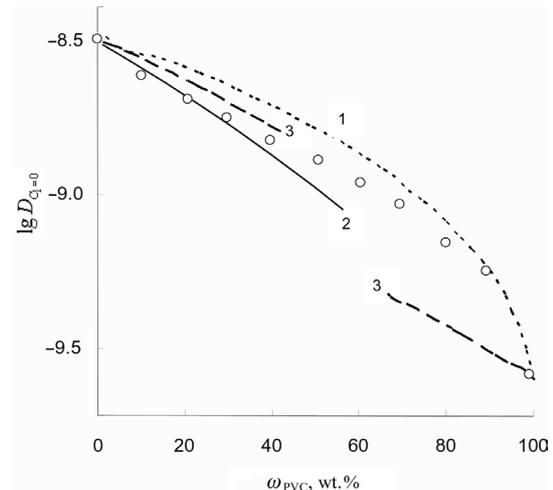
$$D = D_1 \frac{1 + \varphi_2 + 2(1-\varphi_1) D_1/D_2}{1 - \varphi_2 + (2+\varphi_1) D_1/D_2} \quad \text{(Maxwell model),} \quad (7)$$

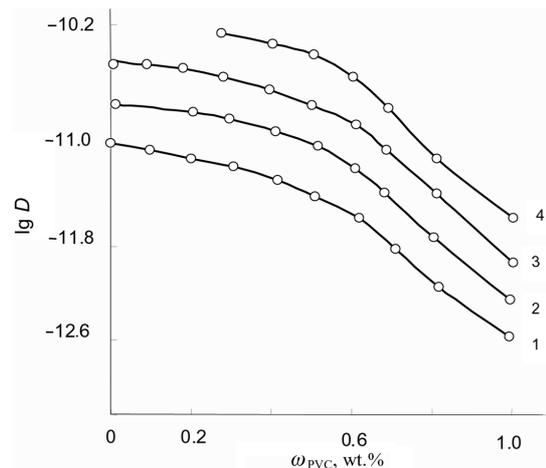$$D = D_1 (1 - \varphi_1^{2/3}) \quad \text{(model for filled composites),} \quad (8)$$

where D_1 and D_2 – diffusion coefficients of the neat polymers, φ_1 and φ_2 – volumetric parts of the neat polymers.

As one can see, the most rapid changes of the diffusion coefficients were observed at CPE contents of up to 20 wt.%, suggesting that phase transition takes place in the low CPE mass content region. The same was observed in our earlier investigations on mechanical and elastic properties of PVC–CPE blends [3,10–12]. In addition, Fig. 7 clearly demonstrates that at low PVC contents experimental data are best described by Eq. (8), and at high PVC contents by Eq. (6).

The described changes of the mass transfer characteristics allow us to assume that different mass transfer mechanisms may govern the diffusion process in the

Fig. 8. Diffusion coefficients (D, m^2/s) of gas penetration in the investigated PVC–CPE compositions at 303 (1), 313 (2), 323 (3), and 333 K (4).

various structural areas of the composites: if the dispersed phase is impermeable to penetrant molecules, the mass transfer properties of the composites are characterized by macroscopic diffusion coefficients and the sorption kinetics is governed by Fick's law [13]. If the matrix and dispersed phase participate in the mass transfer process, diffusion is anomalous [14].

Similarly to the case of low-molecular penetrant diffusion, also gas permeability characteristics depend on the composition, chemical nature, and structure of the base components. For example, with increasing PVC content in the blend, the gas permeability rate gradually decreases, following a soft sigmoidal trend independently from temperature during testing (Fig. 8).

Note that the absolute D values for CPE and PVC differ by 1.5 orders, which agrees with the results obtained by Shur and Ranby [15].

To characterize the dependence of the gas diffusion rate on the composition of the blends, additive (Eq. (6)), Maxwell (Eq. (7)), and Robinson equations were used:

$$D = x_a D_1 \left[\frac{D_2 + 2D_1 - 2\varphi_2(D_1 - D_2)}{D_2 + 2D_1 + \varphi_2(D_1 - D_2)} \right]$$
$$+ x_b D_2 \left[\frac{D_1 + 2D_2 - 2\varphi_1(D_2 - D_1)}{D_1 + 2D_2 + \varphi_1(D_2 - D_1)} \right]$$

$$\text{(Robinson model)}, \quad (9)$$

where D_1 and D_2 – diffusion coefficients of the compatible homopolymers, φ_1 and φ_2 – volumetric parts of the neat polymers.

As it is shown in Fig. 9, the Robinson model is the best for the prediction of the diffusion characteristics of the low-molecular compound in the investigated polymer blends throughout the whole concentration region.

In Fig. 10, activation energies of the diffusion process are shown. Diffusion process activation energies E_D specifically depend on both the composition and structure of the investigated polymer composites. Similarly to the activation energies E_R necessary to induce the flowing process, two different regions of the E_D growth can be distinguished. The emergence of these regions can be explained by the transformations in the macromolecular packing, i.e. density (see Table 1). Consequently, a change in the activation energy values is closely related to (1) the length of the penetrant diffusion path, (2) the amount of the microvoids (most probably created because of the imperfect mixing due to differences in the rheological characteristics of the components), and (3) the relationship of the amounts of permeable and impermeable structural arrangements in the composite.
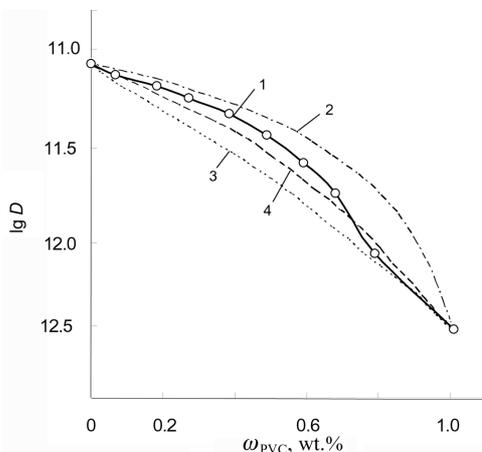
Fig. 9. Mass transfer rate (D, m^2/s) in PVC–CPE compositions at 313 K: 1 – experimental data; 2, 3, 4 – calculations according to Eqs (6), (7), and (9).
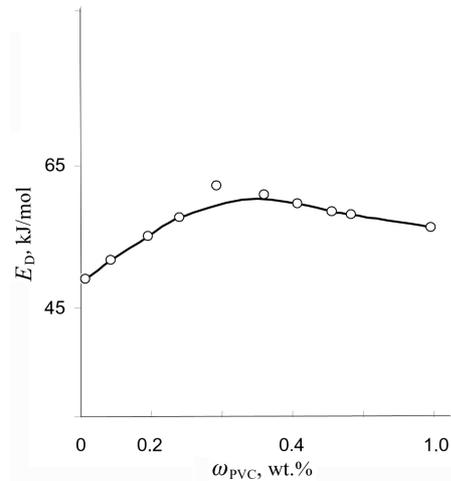
Fig. 10. Change of the diffusion process activation energy of the investigated PVC–CPE compositions.

Table 1. Density of the PVC–CPE compositions

Weight content of the components of the compositions, wt./wt.% PVC:CPE	Experimental density, d_{exp}, g/cm^3	Calculated density, d_{calc}, g/cm^3
0:100	1.170	1.170
10:90	1.168	1.190
20:80	1.190	1.209
40:60	1.229	1.248
60:40	1.274	1.287
70:30	1.294	1.307
80:20	1.320	1.326
90:10	1.348	1.346
100:0	1.365	1.365

CONCLUSIONS

Mass transfer and rheological properties of the binary PVC–CPE blends were investigated. It was concluded from the low-molecular weight compound sorption data and gas permeability analysis that due to their smaller diffusion coefficients, systems with higher PVC content should be regarded as more appropriate for coating and barrier material applications. At the same time diffusion process activation energies specifically depend on both the composition and the structure of macromolecular packing of the investigated polymer composites. Besides, changes of the mass transfer process activation energies are closely related to (1) the length of the penetrant diffusion path, (2) the amount of the micro-voids, and (3) the relationship of the amounts of permeable and unpermeable structural arrangements in the composites. Consequently, it can be concluded that different mass transfer mechanisms can govern the diffusion process in various structural areas of the

investigated composites. In general, the kinetics of the diffusion of low-molecular compounds and permeability of gases depends on the microheterogeneous structure of the investigated PVC–CPE composites as well as on the amount of the microvoids on the interfacial boundary area, locked there during thermoplastic mixing of PVC and CPE.

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Heterogeensed polüvinüülkloriidi segud kloreeritud polüetüleeniga: reoloogilised, difusiooni ja gaassorptsiooni omadused

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On uuritud binaarseid PVC–CPE segusid. Need on valmistatud küllalt laias komponentide vahemikus (PVC/CPE = 100/0, 90/10, 80/20, 60/40, 40/60, 20/80, 10/90, 0/100 massi%. On uuritud nende segude reoloogilisi ja difusiooni omadusi. Sorptsioonanalüüsi andmetest on järeldatud, et pinnakatte- ja barjäärmaterjalides võiks kasutada kõrgema PVC-sisaldusega segusid nende väiksemate difusioonikoefitsientide tõttu. Reoloogilisest analüüsist on järeldatud, et kõik PVC-komposiidid CPE-ga on termoplastilised ja neid võib vormida ning taaskasutada traditsioonilise aparatuuriga.